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Prediction of N_2O emissions under different field management practices and climate conditions

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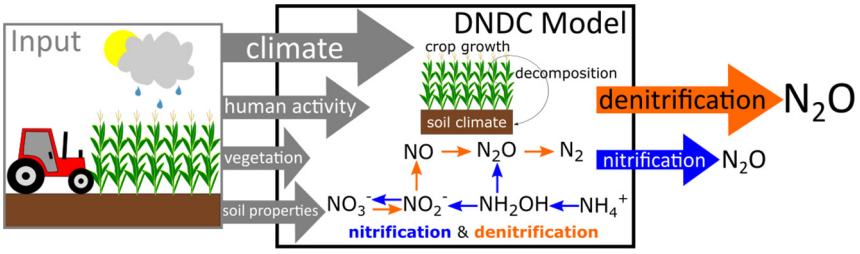
HIGHLIGHTS

- DNDC was evaluated for agricultural N_2O under different management and climates.
- DNDC correctly identified field management that significantly influenced N_2O fluxes.
- DNDC did not predict daily and cumulative N_2O fluxes well, even after calibration.
- N_2O fluxes and model error correlated with precipitation frequency and intensity.
- Model improvements should focus on denitrification surrounding precipitation events.

GRAPHICAL ABSTRACT



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ABSTRACT

Due to the contributions of nitrous oxide (N_2O) to global climate change and stratospheric ozone destruction, it is important to understand how climate and agricultural management affect N_2O emissions. Although the process-based Denitrification Decomposition (DNDC) model is often used for quantifying emissions of N_2O, the accuracy of these predictions remains in question, and it is not clear which input variables, environmental or field management, have the greatest effect on model performance. In this study, DNDC was evaluated for prediction of N_2O fluxes from two climatically-different corn-field sites in the United States (a Colorado irrigated field and a Minnesota rainfed field). Besides climate, these sites offer the additional advantage that measurements are available for multiple field management practices, including fertilizer application, tillage, and crop rotation. This evaluation found that DNDC did not consistently, correctly predict daily-scale N_2O fluxes. Cumulative growing season N_2O fluxes were significantly under-predicted in Colorado and were both under- and over-predicted in Minnesota. Model calibration of four soil input parameters did not significantly improve N_2O emission predictions at either site or time scale. Modeled and measured N_2O fluxes and model error were all strongly correlated with precipitation. Over-predictions of N_2O fluxes were associated with heavy precipitation and high modeled denitrification. Based on our results, model improvements to decrease model error for corn cropping systems in temperate climate zones should focus on better accounting for the effects of precipitation on denitrification. Despite discrepancies in daily and cumulative growing season N_2O fluxes, DNDC correctly identified the only field management (fertilizer application rate) that significantly influenced the measured N_2O fluxes.

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1. Introduction

In the United States, agriculture accounts for 78.9% of nitrous oxide (N_2O) emissions, which contribute to global climate change and ozone depletion (Galloway et al., 2003; USEPA, 2016). Predictive models can help identify locations and times of intense N_2O emissions, compare potential mitigating strategies, and evaluate impacts. Currently, emission estimates are typically based on Tier 1 and/or Tier 3 approaches from the Intergovernmental Panel on Climate Change (IPCC) (IPCC, 2006; USEPA, 2016). The Tier 1 approach estimates direct emissions from agriculture by applying an emission factor of 1% to nitrogen inputs to agricultural soil (IPCC, 2006). However, this emission factor was determined based on only a few studies and has large uncertainty (0.3–3%) (IPCC, 2006). Tier 3 employs process-based biogeochemical models such as the Denitrification-Decomposition (DNDC) model (Li et al., 1992; Li, 2000) and the daily CENTURY (DayCent) model (Parton et al., 1996). Both DNDC and DayCent simulate soil climate, crop growth, decomposition, and nitrogen mineralization and transformation. DNDC was chosen for this study because it was developed specifically for agricultural ecosystems and considers more N pathways than DayCent (Brilli et al., 2017).

To evaluate any of these models, model results are typically compared to field measurements. DNDC has been evaluated for N_2O emissions from different grasslands and cropping systems, including corn, which has one of the highest nitrogen application rates (66–200 kg N ha^{-1}, USDA (2013)). Results relevant to cultivation of corn have been reported for Canada (Uzoma et al., 2015; Abalos et al., 2016; Congreves et al., 2016), China (Li et al., 2010; Cui et al., 2014; Zhang et al., 2015), Belgium (Beheydt et al., 2007), Australia (Chen et al., 2015), and the United States (Deng et al., 2016). Across the various climate zones and field management practices represented in these studies, DNDC's N_2O flux predictions at the daily-scale were typically poor (e.g., Uzoma et al., 2015; Zhang et al., 2015). For annual N_2O emissions, some studies show model calibration can improve quantitative metrics (e.g., root mean square error) and provide estimates within range of measurement uncertainty (Zhang et al., 2015; Abalos et al., 2016), while others report both under- and over-estimation compared to field measurements (Beheydt et al., 2007; Uzoma et al., 2015; Congreves et al., 2016). Since the impacts of N_2O emissions are of a global scale due to its long lifetime, accuracy in annual N_2O emissions is sufficient for certain applications of the model (e.g., annual greenhouse gas emission inventories). However, the need to calibrate the model for each site and the major discrepancies at the daily-scale suggest that DNDC does not fully reflect the processes leading to N_2O emissions; thus, there is a need to identify how the model can be improved.

The DNDC model has been used in a few previous studies to investigate the influence of field management and climate on N_2O emissions from corn fields. These studies report high N_2O flux peaks associated with fertilizer application (Li et al., 2010; Cui et al., 2014; Abalos et al., 2016; Deng et al., 2016), but the influence of other management (e.g., tillage) is less clear. The model seems to be highly sensitive to precipitation (Deng et al., 2016), and N_2O flux predictions often peak after irrigation or heavy rainfall (Li et al., 2010; Cui et al., 2014; Abalos et al., 2016). Of these studies, only a few considered multiple field management combinations in the same study (Cui et al., 2014; Deng et al., 2016), and none have included multiple field management practices simultaneously with different climate and soil conditions. The ability of DNDC to accurately predict the effects of different management practices, climates, and soil conditions on N_2O emissions, therefore, has not been rigorously evaluated.

The aims of this study are to (1) evaluate the DNDC model for N_2O emissions from two U.S. corn cropping systems under multiple field management combinations and different climate conditions, (2) assess model performance before and after model calibration, and (3) determine variables that influence N_2O emissions and DNDC model performance. Previously published N_2O measurement data from three-year corn-field studies in Fort Collins, Colorado (Mosier et al., 2006), and Rosemount, Minnesota (Venterea et al., 2011), were used for model evaluation. By simultaneously considering multiple field management practices in different climate zones, this study contributes to identification of model processes that are contributing to model error.

2. Materials and methods

2.1. Field sites and N_2O measurement data

Two field sites with different climate, soil properties, and field management were chosen to assess the ability of DNDC to predict N_2O fluxes in climatically-different corn-fields in the US. Detailed information about the field sites, including soil properties, field management, measurement methods, and N_2O emissions are available in Mosier et al. (2006) and Venterea et al. (2011) for Colorado and Minnesota, respectively. Climate and soil data are summarized in Table 1. Field management considered in this study included combinations of tillage (conventional (CT) and no-till (NT)), fertilizer application rates, and crop rotations (continuous corn (CC) and corn-soybean (CB)). In Colorado, fertilizer was injected 5 cm below the soil surface as urea ammonium nitrate 32% at: 0 kg N ha^{-1} (0 N), 134 kg N ha^{-1} (134 N), and high nitrogen (202 kg N ha^{-1} in 2002 and 224 kg N ha^{-1} in 2003 and 2004, HN). In Minnesota, fertilizer treatments were broadcast applied at: 4.5 kg N ha^{-1} starter fertilizer (control, C) and 146 kg N ha^{-1} conventional urea (CU). A total of eight different Colorado treatment combinations (CT-CC-0N, CT-CC-134N, CT-CC-HN, NT-CC-0N, NT-CC-134N, NT-CC-HN, NT-CB-0N, and NT-CB-HN) and four different corn-soybean Minnesota treatment combinations (CT-CU, CT-C, NT-CU, and NT-C) were considered. The Minnesota site was exclusively rainfed, while the Colorado site was supplemented with additional irrigation to meet crop water demands. Both sites collected three midmorning gas samples 1–3 times per week using static chambers (Mosier et al., 2006; Venterea et al., 2011). Gas samples were analyzed for N_2O using a gas chromatograph equipped with electron capture detector and fluxes were calculated using linear and nonlinear methods (Mosier et al., 2006; Venterea et al., 2011). The Colorado dataset included year-round measurements, while the dataset from Minnesota only encompassed the growing season. Measured daily N_2O fluxes ranged from 0 to 550 μg N m^{-2} h^{-1} in Colorado and 0 to 170 μg N m^{-2} h^{-1} in Minnesota. Considering all three measurement years together, fertilizer application rate was the only management that significantly influenced N_2O fluxes at both sites.

2.2. DNDC modeling

DNDC (version 9.5, downloaded January 2014) model inputs are ecological drivers, including climate parameters, soil physical properties, vegetation, and anthropogenic activity (Li, 2000). These ecological drivers modify the soil climate (soil temperature, moisture, pH, redox

Table 1
Soil properties and climate for Colorado and Minnesota field sites.

	Fort Collins, CO	Rosemount, MN
Soil texture	Clay loam[b]	Silt loam[a]
Bulk density (g cm^{-3})	1.36[b]	1.45[c]
Soil pH	7.7[b]	6.5[c]
Clay fraction	0.31[c]	0.13[c]
SOC (kg C kg $soil^{-1}$)	0.012[b]	0.028[a]
Average temperature (°C)	10.1[d]	6.9[d]
Average high temperature (°C)	17.6[d]	12.3[d]
Average low temperature (°C)	2.7[d]	1.4[d]
Average annual precipitation (cm)	40.8[d]	88.7[d]

[a] Venterea et al. (2011).
[b] Mosier et al. (2006).
[c] Web Soil Survey (USDA, 2017).
[d] US Climate Data (2017).

potential, and substrate C and N concentrations), which then determines the activity of nitrifiers and denitrifiers in the soil (Li, 2000). For this study, daily temperature and precipitation data for each site and measurement year were based on the nearest climate station data (at a distance of 12 and 4 km for CO and MN, respectively) available from the Department of Natural Resources (2016), the Colorado Climate Center (2017), and The Weather Company (2017). Soil physical properties not found within site publications were obtained from the Web Soil Survey (USDA, 2017). To stabilize soil carbon and nitrogen pools, at least ten years of spin-up time was used based on literature recommendations (Uzoma et al., 2015; Grant et al., 2016). Corn planting dates were based on dates reported in site publications (Halvorson et al., 2006; Venterea et al., 2011), and corn harvest and soybean planting and harvest dates were based on an average of typical date ranges reported by state (USDA, 2010). Since soybean planting and harvest dates were unavailable for Colorado, values were estimated based on those found in Nebraska (USDA, 2010). As exact daily irrigation amounts were not available for the Colorado site, the irrigation index in DNDC was set to 1, allowing crop water demands to be supplemented with additional irrigation when precipitation was low. All other field management data were obtained from site publications (Venterea et al., 2005; Mosier et al., 2006; Halvorson et al., 2008; Halvorson et al., 2010; Venterea et al., 2011).

For this study, the model output of interest was daily N_2O flux, which can be produced by nitrification and denitrification. In DNDC, N_2O production from nitrification and denitrification is controlled by soil moisture, temperature, pH, and substrate concentrations, all of which are calculated by DNDC based on input parameters. The daily N_2O fluxes were summed during the growing season of each year to calculate the cumulative measured N_2O emissions during the growing season. Model uncertainty in cumulative N_2O fluxes was estimated using Monte Carlo simulations based on uncertainty in precipitation input data (described in the Supplementary information, Section S1 and Table S1). For summation of measurement data, linear interpolation was used to obtain daily N_2O fluxes between measurement dates and uncertainty in this interpolation method was estimated based on the average interval between sampling dates (Parkin, 2008). For all quantitative analyses, cumulative measured N_2O emissions during the growing season were compared to model predictions. Unless specifically identified as calibration results, all model results are based on the default model.

In addition to running the default model, DNDC was calibrated through parameter optimization (Smith and Smith, 2007) of soil parameters to obtain the best model agreement with cumulative growing season N_2O flux measurements. Initially, six soil parameters (pH, clay content, soil organic carbon (SOC), bulk density, field capacity, and wilting point) were chosen based on the availability of site-specific initial values and a literature review, which revealed that these soil parameters were most influential for N_2O fluxes (Ludwig et al., 2011; Rafique et al., 2011; Deng et al., 2016). Uncertainty ranges (Table 2) were calculated from the range of values found in the vicinity of the field site using the Web Soil Survey (USDA, 2017) or from uncertainty estimated in the literature (Twarakavi et al., 2009). However, sensitivity analysis (described in the Supplementary information) showed low sensitivity of N_2O fluxes to soil bulk density and wilting point, so the number of parameters for optimization was reduced to four. All results reported from calibrated models are therefore based on optimization of pH, clay content, SOC, and field capacity. Initially, the model was calibrated for one field management condition and validated across other field management practices. However, the calibrated models did not improve predictions for other management at the same site (data not reported). Instead, the model was calibrated for each field management individually, based on the first year of field measurements, and then validated by comparison to subsequent years of field measurements under the same management.

Table 2
Parameters used in model calibration and ranges tested by parameter optimization.

Parameter	Fort Collins, CO	Rosemount, MN
pH	7.2–8.2	6–7
Clay content (%)	21–31	8–18
SOC (g kg^{-1})	7.5–17.5	25–35
Field capacity (%)	47–67	30–50

2.3. Statistical analyses

The following quantitative metrics were used to evaluate how well DNDC predicted the measured N_2O emissions: zero-intercept linear regression (slope and coefficient of determination), root mean square error (RMSE), model efficiency, and model error. Zero-intercept linear regression between modeled and measured cumulative growing season emissions, including slope and the coefficient of determination (R^2), was completed in OriginPro (OriginLab, 2017). Overall normalized RMSE was calculated by Eq. (1), with a value of 0% indicating good model fit (Smith and Smith, 2007). Model efficiency was calculated using Eq. (2), with a value of 1 indicating good model fit (Smith et al., 1997). Model error for each treatment and year was calculated by Eq. (3) and used in subsequent correlation analyses.

$$RMSE(\%) = \frac{100}{\overline{O}}\sqrt{\frac{\sum_{i=1}^{n}(P_i - O_i)^2}{n}} \quad (1)$$

$$model\ efficiency = \frac{\sum_{i=1}^{n}\left(O_i - \overline{O}\right)^2 - \sum_{i=1}^{n}(P_i - O_i)^2}{\sum_{i=1}^{n}\left(O_i - \overline{O}\right)^2} \quad (2)$$

$$error = \frac{|P_i - O_i|}{O_i} \quad (3)$$

In Eqs. (1)–(3), O_i is the ith measured value, P_i is the ith modeled value, n is the number of values compared, and $\overline{O}$ is the average measured value.

The original measured and modeled data and their log transformations were tested for normality by the Shapiro-Wilk test. Equality of variance was tested by the Bartlett test and Levene test for normal and nonnormal data, respectively. In all cases, at least one assumption (normality or equality of variance) was violated, for one or both sites, so nonparametric tests were used to test for statistical significance. To determine if modeled and measured cumulative growing season emissions were significantly different, the Wilcoxon Signed-Rank test was used on data from each site. The influence of treatments on measured and modeled N_2O flux was assessed by the Kruskal-Wallis test, which tests for variance between the levels of each treatment (e.g., comparing conventional tillage and no-till). Unless otherwise specified, all statistical analyses were computed in R (R Core Team, 2013) with significance for $P < 0.05$.

Correlation statistics were used to determine variables that influence modeled and measured N_2O fluxes and model performance. In these tests, model error was used as an assessment of model performance and was calculated by Eq. (3). The Spearman's Rank Correlation test was used to calculate rho values (−1,1). Values of rho near 1 or −1 indicate strong positive or negative correlations, while values near 0 indicate no correlation. Modeled and measured N_2O fluxes were tested against maximum and minimum temperature, daily precipitation, and weekly precipitation (the sum of precipitation in the week prior to the tested day). Model performance was tested against several variables related to precipitation, including annual precipitation, annual precipitation in the previous year, percentage difference between annual precipitation and average annual precipitation, and number of high magnitude precipitation events (>3 cm, >4 cm, and >5 cm).

3. Results

3.1. Daily-scale N_2O fluxes

In Colorado, daily-scale N_2O fluxes were over- or under-predicted (Fig. 1 shows two treatments; other treatments shown in Figs. S1 & S2). Over-predictions mainly occurred during 2003 and on two specific days (78 and 243). On day 78 of 2003, 40 days before fertilization, model N_2O fluxes were as high as 550 μg N m^{-2} h^{-1} (Figs. 1, S1, and S2) while measured values were <10 μg N m^{-2} h^{-1} on days close to this modeled peak. Similarly, unfertilized plots had relatively large modeled N_2O flux peaks (82–113 μg N m^{-2} h^{-1}), while measured N_2O flux remained near zero. Temperatures in the days before the model N_2O flux peak were above freezing and two high-magnitude precipitation events of 8.4 and 4.1 cm had occurred on days 77 and 78, respectively. Later in 2003, on day 243, there was a second modeled N_2O flux peak that did not correspond to any measured flux peak. This peak occurred the day after a high-magnitude precipitation event of 6.3 cm. Comparison to model outputs of nitrification and denitrification activity indicated that both over-prediction N_2O peaks correspond to peaks in denitrification (Fig. S3). Significant under-predictions of N_2O fluxes occurred in fertilized plots during the month following fertilization. Modeled N_2O fluxes were 1–2 orders of magnitude lower than measured N_2O fluxes (100–550 μg N m^{-2} h^{-1}). This under-prediction was observed for most fertilized plots and years, although the greatest discrepancies were again observed in 2003. During the time following fertilization, the model outputs showed increases in both nitrification and denitrification (Fig. S3); it is not clear whether one or both processes are being under-predicted. Generally, both modeled and measured N_2O fluxes were low in unfertilized plots, and conventional tillage N_2O fluxes were better predicted than those in no-tillage plots (Figs. S1–S2). The worst prediction year (2003) had more high-magnitude (>3 cm d^{-1}) precipitation events (10) than other years (1 and 0 in 2002 and 2004, respectively).

In Minnesota, daily-scale N_2O fluxes were also under- or over-predicted (Fig. 2 shows two treatments; all treatments shown in Fig. S4). Model N_2O flux under-predictions were less extreme than over-predictions and were of a similar magnitude as compared to measurements. Two unusually high N_2O peaks occurred during 2010, on days 91 and 226. On day 91 of 2010, 39 days before fertilization, model N_2O fluxes were between 250 and 3450 μg N m^{-2} h^{-1}. Measurements had not been taken during that period, as fluxes were expected to be low prior to fertilization. Leading up to day 91, temperatures were 10–20 °C above freezing. No significant precipitation events occurred, but there had been steady snow accumulation over the winter, so snowmelt could have contributed. Later, on day 226 of 2010, model over-predictions were as much as two orders of magnitude higher than measurements, with N_2O flux peaks as high as 1100 μg N m^{-2} h^{-1} when measurements were <25 μg N m^{-2} h^{-1}. Both unexpected N_2O flux peaks (day 91 and 226) coincided with model predicted denitrification peaks, while the expected peaks shortly after fertilization corresponded to modeled peaks in nitrification and some denitrification (Fig. S5). Generally, N_2O fluxes were better predicted in 2008 and 2009, while modeled N_2O flux predictions were over-predicted in 2010. Comparing meteorological data from these three years, 2010 was the first year with near-average precipitation (83 cm y^{-1}) after several years of drought (<58 cm y^{-1}). In addition, 2010 had more high-magnitude (>3 cm d^{-1}) precipitation events (10) than previous years (7 and 1 in 2008 and 2009, respectively). Overall, at both sites, DNDC poorly predicted daily-scale N_2O fluxes.

3.2. Cumulative growing season N_2O fluxes

To evaluate whether DNDC could accurately predict annual N_2O fluxes, despite its difficulty in predicting them at the daily-scale, the measured and modeled values for cumulative N_2O flux over the growing season were also compared using zero-intercept linear regression plots. In Colorado, the model consistently under-predicted cumulative growing season N_2O fluxes (Fig. 3, top). Unfertilized plots had modeled cumulative growing season N_2O fluxes of 0.03–0.14 kg N ha^{-1}, while measurements were 0.14–0.78 kg N ha^{-1}. Fertilized plots had modeled cumulative growing season N_2O fluxes of 0.19–0.77 kg N ha^{-1}, while measurements were 0.51–3.41 kg N ha^{-1}. Considering all treatments and years in Colorado, fluxes were significantly different between modeled and measured (Wilcoxon Signed-Rank, $P < 0.001$). Including ranges of uncertainty due to precipitation for modeled N_2O flux and due to linear interpolation for measured N_2O fluxes, the model was successful in predictions of 17% of the Colorado measurements. In Minnesota, the difference was not significant between modeled and measured cumulative N_2O fluxes (Wilcoxon Signed-Rank, $P = 0.519$), as the model sometimes under-predicted and sometimes over-predicted cumulative growing season N_2O fluxes (Fig. 3, bottom). In

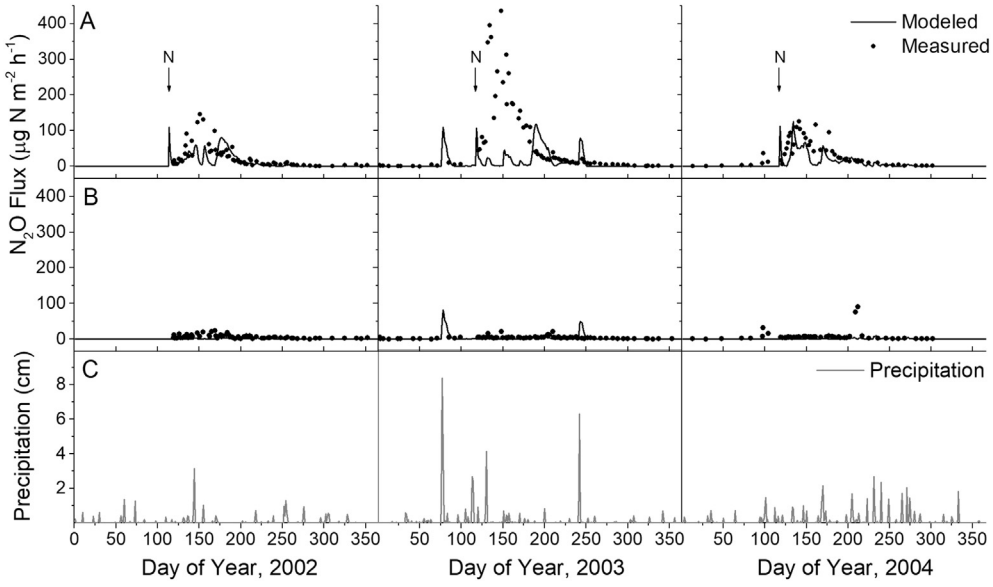

Fig. 1. Colorado daily-scale modeled and measured N_2O fluxes (A, B) and precipitation (C) for continuous corn crop rotations with conventional tillage from 2002 to 2004. Panel (A) shows a fertilized plot (CT-CC-HN), where arrows indicated dates of fertilization, and panel (B) shows an unfertilized plot (CT-CC-0N).

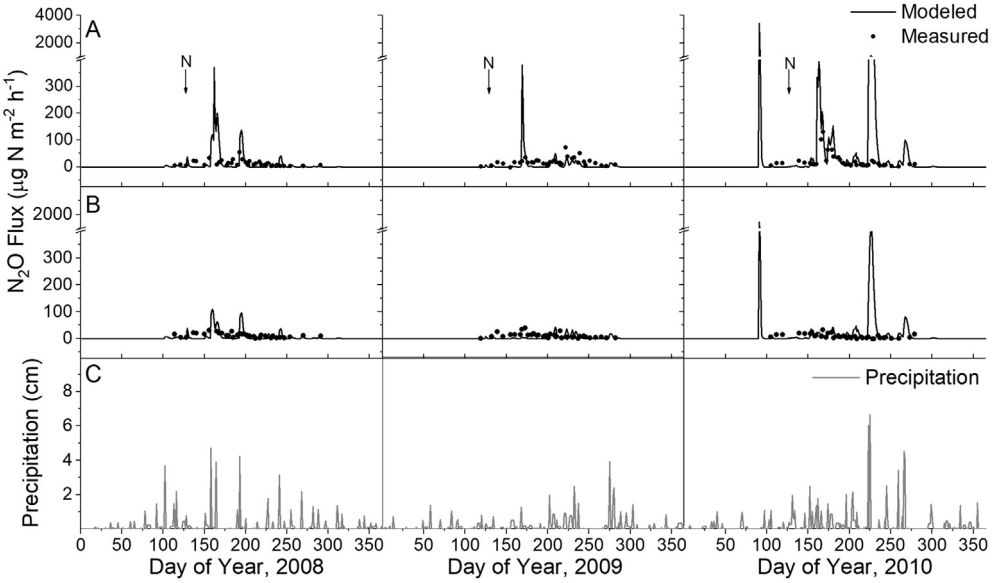

Fig. 2. Minnesota daily-scale modeled and measured N_2O fluxes (A, B) and precipitation (C) for corn years of a conventionally tilled corn-soybean crop rotation from 2008 to 2010. Panel (A) shows a fertilized plot (CT-CU), where arrows indicated dates of fertilization, and panel (B) shows an unfertilized plot (CT-C). Note the line break, occurring from 400 to 1000 μg N m^{-2} h^{-1}.

2008, the model under- or over-predicted N_2O fluxes, but fluxes were of similar magnitudes compared to measurements. In 2009, the model consistently under-predicted N_2O fluxes, especially in unfertilized plots. In 2010, model predictions were more than twice the measured values for all plots. Including ranges of uncertainty due to precipitation for modeled N_2O flux and due to linear interpolation for measured N_2O fluxes, the model was successful in predictions of 58% of Minnesota measurements. Despite Minnesota's measured and modeled cumulative growing season N_2O fluxes not being significantly different, the overall model performance was worse in Minnesota, with a higher

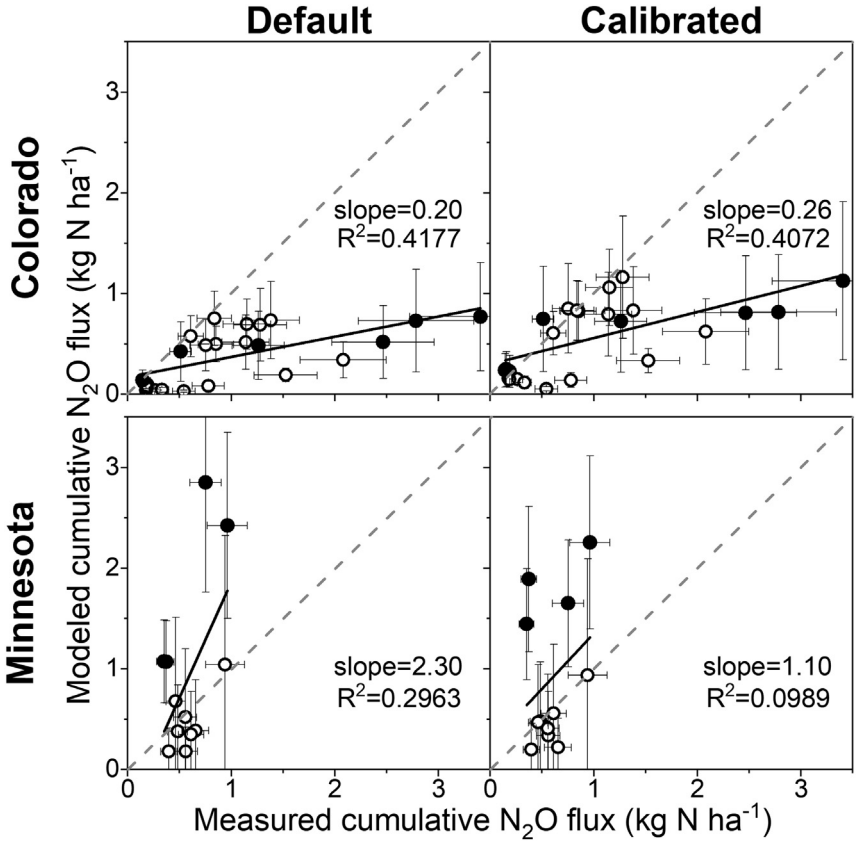

Fig. 3. Comparison of modeled versus measured cumulative N_2O flux graphs before and after calibration for Colorado (CO) (top) and Minnesota (MN) (bottom). Each point represents the cumulative N_2O flux for a different combination of treatment and year. Symbols highlight high precipitation years: solid circle - heavy precipitation years (CO 2003, MN 2010), open circle - other years. Error bars are standard deviations based on model or measurement uncertainty. Grey dashed line represents the 1:1 line that would be expected from a perfect fit; points above and below this line are over- and under-predicted cumulative growing season fluxes, respectively.

RMSE and a lower model efficiency, as compared to Colorado (Tables 3 & S3).

Given this poor performance at both sites, we also tested the potential to improve DNDC's performance through calibration, specifically using parameter optimization on pH, clay content, SOC, and field capacity. By zero-intercept linear regression, R^2, and slope, calibration did not dramatically improve model performance at either site (Fig. 3). Although calibration improved RMSE and model efficiency at both sites, calibrated model performance was still poor (Tables 3 & S3). Considering ranges of uncertainty due to precipitation for modeled N_2O flux and due to linear interpolation for measured N_2O fluxes, the calibrated model for Colorado led to an increase to 42% for successfully predicted management and year combinations. However, when considering this uncertainty in Minnesota, the calibrated model did not improve prediction success.

3.3. Field management

Considering the impact of field management on N_2O flux, DNDC correctly identified those treatments that were previously reported as significant based on the measurements (Mosier et al., 2006; Venterea et al., 2011). In both Colorado and Minnesota, fertilizer application significantly increased modeled and measured N_2O fluxes (Kruskal-Wallis, $P < 0.01$ for all tests). Tillage had no significant effect on modeled and measured fluxes (Kruskal-Wallis, $P > 0.3$ for all tests). In Colorado, where crop rotation was tested, rotation did not significantly affect modeled and measured N_2O fluxes (Kruskal-Wallis, $P > 0.1$ for all tests).

3.4. Correlations with environmental parameters

Correlation analysis was completed to determine variables that might influence modeled and measured N_2O fluxes and model performance. Modeled and measured N_2O fluxes were positively correlated with temperature and precipitation in Colorado and Minnesota, with stronger correlations exhibited by the model (Table S4). Weekly precipitation was more strongly correlated with N_2O fluxes than daily precipitation. Model error was not strongly correlated with any precipitation variables when considering both sites together (Table 4). However, separating the two sites, Minnesota had strong correlations between model error and all precipitation variables tested. Model error was positively correlated with precipitation and the number of high-magnitude precipitation events in the model year, suggesting that increased precipitation increases model error. Model error was also negatively correlated with precipitation in the previous year, meaning that as precipitation decreases in the previous year (i.e., drought) model error increases.

4. Discussion

To be useful for identifying ways to reduce N_2O fluxes while maintaining crop yields, a biogeochemical model should be capable of i) reasonably predicting N_2O fluxes, including temporal trends and annual magnitudes, and ii) capturing any significant differences between management practices of interest. In this study, the DNDC model poorly predicted daily-scale N_2O fluxes, both under- and over-predicting fluxes, especially in years with high frequency and magnitude of precipitation. Considering cumulative growing season N_2O fluxes, DNDC significantly under-predicted N_2O fluxes in Colorado and both under- and over-predicted N_2O fluxes in Minnesota, again with the worst predictions in years with high precipitation. Drought conditions in the previous year also correlated with high model error, as evident in the unirrigated Minnesota site. However, despite these discrepancies in predicted fluxes, DNDC accurately identified the only tested management that significantly influenced N_2O fluxes in the measured data: the fertilizer application rate.

The parameter optimization calibration technique used in this study did not improve the DNDC model's predictions enough to warrant the effort required. Some previous studies similarly reported inconsistent predictions even after calibration (Beheydt et al., 2007; Uzoma et al., 2015; Congreves et al., 2016). However, other studies have obtained reasonable N_2O emission predictions after calibration, at least at the annual scale (Ludwig et al., 2011; Cui et al., 2014; Abalos et al., 2016; Deng et al., 2016). Of those studies that were successful, at least two of them used a data-intensive multi-level calibration approach (Ludwig et al., 2011; Abalos et al., 2016), which requires year-round field measurements of additional variables (e.g., water filled pore space). Although the multi-level calibration approach allowed for better N_2O flux predictions for the site it was calibrated for, it could not be applied to the datasets used here due to variables that were not measured, which was a limitation of this study. These intense calibration methods are likely not practical for use in policy and decision-making models due to the amount of data required. It is important to note that these difficulties are not restricted to DNDC, as studies using other models have reported similar difficulty with N_2O flux predictions (Brilli et al., 2017; Gillette et al., 2017).

Investigating the source of the poor model predictions obtained here, we identified historic and current year precipitation as important parameters, with drought in previous years and heavy precipitation in the current year both corresponding to years with greater model error. To our knowledge, a relationship between historic precipitation conditions and model error has not been reported previously. Generally, increases in model error could be derived from high uncertainty in input parameters, inaccurate predictions of underlying drivers such as soil organic carbon (SOC), soil N, or soil moisture, or from difficulty in modeling the microbial response to these situations. Although the precipitation input had considerable uncertainty in this study, the resulting uncertainty in N_2O fluxes could not always account for the discrepancy in modeled and measured emission, especially during years with heavy precipitation. Considering predictions of soil parameters, the model predicted decreases in SOC by about 1% following drought. A DNDC sensitivity study found SOC to be the main factor influencing N_2O fluxes, with increases in SOC by as little as 0.25%–2% accounting for an increase of up to 22 kg N ha^{-1} y^{-1} (Li et al., 2010). However, that relationship could not account for the results observed here,

Table 3
Default and calibrated model root mean squared error (RMSE) as a percent and model efficiency (ME) for Colorado and Minnesota based on comparing cumulative growing season N_2O flux between measurements and model predictions across all management practices and years.

	RMSE (%)	ME
CO default	94.4	−0.26
CO calibrated	81.1	0.07
MN default	137.4	−16.11
MN calibrated	122.0	−12.53

Table 4
Model error rho values calculated by Spearman's Rank Correlation test for Colorado and Minnesota across all treatments. Absolute values >0.5 are bolded.

	Colorado	Minnesota	CO and MN
n=	24	12	36
Precipitation (cm y^{-1})	−0.0255	**0.6504**	0.1516
Irrigation (cm y^{-1})	−0.0885	N/A	−0.1019
Total water, precipitation + irrigation (cm y^{-1})	−0.1327	**0.6504**	0.2763
Previous year precipitation (cm y^{-1})	0.2212	**−0.8193**	0.0390
Previous year total water (cm y^{-1})	0.2212	**−0.8193**	0.0695
Difference between average and actual precipitation (cm y^{-1})	0.0255	**−0.6504**	−0.1896
Difference between average and previous year precipitation (cm y^{-1})	−0.2212	**0.8193**	0.0653
No. high-magnitude precipitation events (>3 cm)	−0.2212	0.3073	0.0400
No. high-magnitude precipitation events (>4 cm)	−0.2043	**0.6504**	0.0376
No. high-magnitude precipitation events (>5 cm)	−0.2043	**0.8193**	0.2382

where lower SOC was predicted in the same year as increases in N_2O fluxes. This suggests that SOC is not driving the increased model error. Considering soil N, we observed that drought years had lower predicted crop N uptake and soil N losses, resulting in higher predictions of soil NO_3^- remaining at the end of the drought period as compared to non-drought years (data not shown). Higher soil NO_3^- would provide more substrate for denitrification, accounting for increased N_2O production in the model when precipitation returned to normal or above normal levels. These modeling results were consistent with measured soil NO_3^- reported for 2008, which was significantly higher than in subsequent years (Venterea et al., 2011), suggesting that model error is not from inaccurate predictions of soil N. A recent review also attributed many of the issues with DNDC-based predictions of N_2O to inaccurate predictions of soil moisture or interactions between rainfall and soil properties (Brilli et al., 2017). However, in a study that calibrated the model to match measured soil moisture data, N_2O flux predictions were not improved (Ludwig et al., 2011). Taken together, these results suggest that there are problems with the modeling of both soil moisture and the microbial response to precipitation. Until these problems are resolved, N_2O flux results from DNDC during years of heavy precipitation should be interpreted with caution, especially if the previous year had drought conditions.

At the daily scale, our model results included some unexpected, high N_2O fluxes that were either outside the measurement period or did not correspond to measured peaks. Many of these occurred in late winter or early spring, more than a month before fertilization, and resulted from increases in predicted denitrification induced by elevated precipitation or spring thaw. In Colorado's year-round measurement campaign, N_2O fluxes were consistently low before fertilization, suggesting that these peaks are artifacts of the model. However, no corresponding data were available from Minnesota. Furthermore, there is some evidence for N_2O peaks associated with spring thaws, so it is possible that the model's early spring peaks in Minnesota are real. For example, using DNDC after validation with data from 23 Canadian field studies, a modeling study indicated that spring thaw N_2O peaks are significant and may account for 30% of annual N_2O emissions (Smith et al., 2004), which led to development of a Canadian version of DNDC that accounts for the effect of freeze/thaw in cold climates (Uzoma et al., 2015). As Minnesota experiences colder temperatures than Colorado, it is possible that spring thaw induced N_2O peaks exist in Minnesota, similar to those found in cold climate field studies. Yet, the magnitudes of the model predicted freeze/thaw N_2O peaks reported here are 3–12 times higher than those reported in previous field studies (Goodroad and Keeney, 1984; Burton and Beauchamp, 1994), suggesting that denitrification-induced freeze/thaw N_2O peaks are indeed over-predicted by DNDC in this study.

At both sites in mid-summer of high precipitation years, when soil N and N_2O emissions are expected to be low, we observed another unexpected N_2O peak. This peak also coincided with high magnitude precipitation and high modeled denitrification rates. Although high N_2O fluxes are generally thought to be associated with the co-occurrence of fertilizer and precipitation, there is some evidence from field studies that N_2O flux peaks can be associated with high magnitude precipitation alone (Baggs et al., 2003), including the study that provided the measurements used here (Venterea et al., 2011). However, the modeled N_2O fluxes associated with heavy precipitation were 2–10 times higher than those reported in these field studies, suggesting again that the N_2O predictions associated with precipitation may exist, but are currently over-estimated by the model. A recent study observed a similar phenomenon of denitrification-based over-predictions from DNDC in a different climate and cropping system (Deng et al., 2018), suggesting that the problem may be widespread. Interestingly, a study using the same measurement data from Colorado as was used here, but with the RZ-SHAW model, also had over predictions of N_2O fluxes, but these were due to nitrification peaks (Gillette et al., 2017).

An increase in denitrification during extreme precipitation events is consistent with the known effect of soil moisture on denitrification (Firestone and Davidson, 1989). However, based on a close inspection of the DNDC model algorithm, we identified two possible explanations for the over-prediction of N_2O fluxes, both of which restrict the final step of denitrification (N_2O to N_2). First, the DNDC version used here appears to completely shut down N_2O reduction during extreme precipitation events, such that denitrification ends at N_2O rather than N_2. There is some support for this from laboratory experiments with soil drying and rewetting, where a transient increase in the mole fraction of N_2O to ($N_2O + N_2$) has been reported upon rewetting (Mulvaney and Kurtz, 1984; Dendooven et al., 1996; Jacinthe et al., 2000; Bergsma et al., 2002; Guo et al., 2014). However, the magnitude and duration of this increase seem to vary greatly, with mole fractions ranging from 0.1–0.95 and times ranging from a few hours to days, depending at least in part on the extent of drying, the degree of rewetting, and the land use history (Dendooven et al., 1996; Bergsma et al., 2002; Guo et al., 2014). A better understanding of the relationship between precipitation and the mole fraction of N_2O produced from denitrification, and incorporation of this understanding into DNDC, could improve model predictions. An alternative explanation is that the increase in N_2O flux relates to substrate availability. Denitrification proceeds step-wise in DNDC, so that substrate is used by each reduction step in order (Li, 2000). As the Minnesota site had lower SOC in 2010, it is possible the carbon substrate apportioned to denitrification was consumed before denitrification reached the final step, preventing further reduction to N_2.

5. Conclusions

In both datasets considered here, fertilizer had a significant effect on N_2O fluxes, while tillage and crop rotation did not. The DNDC model accurately identified those management effects. However, N_2O flux predictions at both the annual and daily-scale were poor, including both under- and over-predictions, even after calibration and consideration of model uncertainty from input parameter uncertainty. Precipitation was an important factor influencing the observed and simulated N_2O emissions and model error. Model performance was worst in the years of high magnitude and frequency precipitation, especially after several years of drought for the rainfed site. This is particularly concerning, as it suggests increased uncertainty around N_2O flux predictions under the more frequent extreme weather events expected as climate change continues.

While more complex calibration approaches might improve model performance, our recommendation is to improve the default model's formulation. Specifically, based on the analysis presented here, focus should be on accounting for the influence of precipitation on microbial components of the model: the denitrification rate and N_2O reduction to N_2. In addition, further assessment may be required for the method of substrate allocation based on redox potential. Such improvements need to be supported by targeted field research that provides more data from drying/rewetting and freeze/thaw events, to permit development of a more accurate representation of these processes in DNDC. In this way, the model can provide more reliable predictions of the effects of modifying field management and changing climate on N_2O fluxes, supporting agricultural management decisions and greenhouse gas predictions across the planet.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2018.07.364.

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